

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room B113 - Session HC+SS-FrM

Greatest Hits in Heterogeneous Catalysis

Moderators: Liney Arnadottir, Oregon State University, Ashleigh Baber, James Madison University, Dan Killelea, Loyola University Chicago

8:20am **HC+SS-FrM-1 CO Characterized Pt/Cu(111) Single Atom Alloy (SAA) for the Hydrogenation of Unsaturated Aldehydes, David Molina, M. Trenary, University of Illinois - Chicago**

The use of heterogeneous catalysts is of high importance in a vast number of industrial processes. A promising new type of heterogeneous catalyst known as single atom alloys (SAAs) greatly reduce the amount of precious metal (e.g. Pt, Pd, Rh, Ru) used and have shown enhancements in selectivity, when compared to their pure counterparts, in various types of reactions, including hydrogenation reactions. Hence, it is important to be able to quantify the amount of precious metal on the surface of these catalysts and understand their properties. We have used reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) of adsorbed CO were used to probe the properties of Pt/Cu(111) surfaces, ranging from a multilayer film of Pt on Cu(111) to 2% Pt/Cu(111). For Pt deposition on Cu(111) at room temperature, the Pt coverage was varied from a multilayer film to 0.23 monolayer (ML). As the Pt coverage decreased, a RAIR C–O stretch peak in the range of 2041–2050 cm^{-1} showed isolated Pt atoms embedded in the Cu(111) surface. Pt islands were identified by a C–O stretch peak in the range of 2058–2067 cm^{-1} , showing CO on top of Pt atoms. These islands also allowed for CO to bind at bridge sites between two Pt atoms and this was supported by the observed C–O stretch peak at 1852 cm^{-1} . Deposition of low coverages of Pt at 380, 450 and 550 K formed SAAs in which surface Pt is only present as isolated atoms that had replaced Cu atoms in the topmost atomic layer, in agreement with previous studies with scanning tunneling microscopy. Adsorption of CO on top of the Pt atoms of the SAAs leads to a C–O stretch in the range of 2041–2046 cm^{-1} . Compared to the SAA formed by Pt deposition at 380 K, deposition at 450 and 550 K led to more dispersed Pt atoms as indicated by the lack of a shift of the C–O stretch peaks, indicating that the distance between CO molecules was not low enough for dipole-dipole coupling shifts to occur. In all cases, the C–O stretch of CO on the Pt atoms of Pt/Cu(111) was significantly redshifted relative to its value on Pt(111), which is a manifestation of how nearby Cu atoms alter the Pt–CO bonding. The well characterized Pt/Cu(111) SAA is currently being used to study the hydrogenation of model unsaturated aldehydes.

8:40am **HC+SS-FrM-2 Efficient Catalyst and Protection Layer of Ni/ α -Al₂O₃ Catalysts for Improved H₂O/CO₂ Reforming Reaction of CH₄ via Atomic Layer Deposition, Dae Woong Kim, H. Jeong, W. Hong, J. Park, S. Oh, J. Jang, Hyundai Motor Company, Republic of Korea**

Recently, production of synthetic gas by combined steam and CO₂ reforming reaction of CH₄ (CSCR) is proposed for dealing with the energy problem. In the CSCR process as methane reforming reaction, the synthesis of steam (H₂O), CH₄, and CO₂ occurs at high temperatures and pressures in the presence of metal catalysts. [1] In general, Ni-based catalysts are attractive materials because of their relatively high activity and low cost as compared to noble metal catalysts. [2] As a support structure, a thermally stable, acid-free and inert α -Al₂O₃ is a well-known material. [3] However, catalytic pellets through mixed powder sintering have low structural strength as well as poor catalytic utilization due to dead nickel volume. Therefore, atomic layer deposition (ALD) is proposed as a reliable and atomic scale-adjustable process for conformally growing NiO on α -Al₂O₃ surface with an exact thickness. In the case of ALD-based catalyst growth, the reaction efficiency can be maximized without a catalyst dead area because the catalyst is formed only on the active surface where the reforming reaction can occur.

In this work, ALD NiO film was grown on α -Al₂O₃ pellet supporter which is followed by reduction annealing for highly active CSCR reforming catalyst with a low Ni concentration. Furthermore, an ultra-thin Al₂O₃ protection layer was proposed to enhance stability and coking resistant of Ni/ α -Al₂O₃ catalyst during reforming reaction. Detailed experimental results will be presented.

[1] Energy Fuels 2015, 29, 1055–1065

[2] RSC Advanced 2015, 5, 7539–7546

[3] Journal of Energy Chemistry 22(2013)919–927

[4] Catalysis Science & Technology 2020, 10, 8283

9:00am **HC+SS-FrM-3 Complementary Outer Atomic Layer Analysis of Catalyst Materials Using LEIS, P. Brüner, IONTOF GmbH, Germany; J. Järvillehto, Department of Chemical and Metallurgical Engineering, Aalto University School of Chemical Engineering, Finland; S. Saedy, Chemical Engineering Department, Delft University of Technology, Netherlands; Thomas Grehl, IONTOF GmbH, Germany**

Performance of material in heterogeneous catalysis is dominated by the composition and chemical state of the outer atomic layer. A number of techniques successfully characterize the material at and close to the surface (e.g. XPS) or directly the interaction of the gas phase with the surface (operando techniques, e.g. IR). Also, physical properties like specific surface area are determined. However, Low Energy Ion Scattering (LEIS) is the only technique capable of determining specifically the elemental composition of the outer atomic layer. This opens a range of possibilities to learn about the materials and especially the preparation of catalysts. Due to the high sensitivity of LEIS, this can be performed on both model as well as industrial catalysts.

In this contribution, we will highlight a range of catalysis applications of LEIS on very different materials. This includes nanoparticles and their catalytically active phase on the surface of these particles, and how this surface changes depending on the environment, e.g. a calcination procedure. This can be a dispersed Pt phase and the prevention of sintering by ALD coating. Also industrial particles used for low cost catalysts are shown, specifically the behavior of the active Fe phase and reorganization of the surface under calcination. Another example is demonstrating the Pt deposition inside porous Al₂O₃ beads using ALD [1], and how LEIS analysis can help to optimize the process.

Common to all examples is the specific view that LEIS allows due to its single atomic layer information depth, complementing the information gathered from the many other (surface) analytical techniques applied to catalyst materials.

[1] J. Järvillehto, Thesis, Aalto University, <https://aaltoodoc.aalto.fi/handle/123456789/119352>

9:20am **HC+SS-FrM-4 Size-Selected Pt_n Cluster Electrocatalysts for Alcohol Oxidation, Zihan Wang, University of Utah, China; T. Masubuchi, University of Utah, Japan; M. O'Brien, S. Anderson, University of Utah**

Alcohol oxidation is catalyzed by size-selected Pt_n clusters deposited on indium tin oxide (ITO) and highly oriented pyrolytic graphite (HOPG) electrodes is being investigated. Clusters are generated in the gas phase, mass selected, then deposited on the electrode supports under controlled conditions, in UHV. Electrocatalysis is studied using a unique *in situ* system that allows aqueous electrochemistry to be studied in an antechamber on the UHV system, without exposure to air. Based on cyclic voltammetry (CV), the activity and selectivity for oxidation of 1- and 2-propanol are strongly dependent on cluster size, for Pt_n/ITO, and the activity is correlated with Pt core level binding energies measured by XPS. For HOPG, high activity has been observed for both soft- and hard-landed clusters, and the challenge is to understand the nature of the Pt–HOPG binding for cluster prepared under different conditions. Preliminary data shows that even HOPG, which has weak bonding with Pt, can preserve the deposited cluster size long enough to give size-dependent electrocatalysis, if the clusters are deposited under conditions that pin them to the support. The results for propanol oxidation are expected to provide insight into primary vs. secondary alcohol oxidation in glycerol, which is important for upgrading biobased glycerol into commercial products.

9:40am **HC+SS-FrM-5 Calorimetric Energies of Metal Atoms within Nanoparticles on Oxide and Carbon Supports: Improved Size Dependencies, Adhesion Energies and Trends versus Metal Element with the Spherical Cap Model, Kun Zhao, University of Washington; D. Auerbach, Max Planck Institute for Multidisciplinary Sciences, Germany; C. Campbell, University of Washington**

The chemical potential of metal atoms in supported nanoparticles is an important descriptor of their catalytic performance that captures the effects of particle size and support. Previously, we used the hemispherical cap model (HCM), which assumes 90 degree contact angle of nanoparticles, to model the chemical potential versus size of the nanoparticles. The HCM has been successful in predicting the chemical potential increase with the decreasing of particle size and gives linear trends of adhesion energy with the metal oxophilicity or carbophilicity per unit area for the metal nanoparticles on oxide or carbon supports, respectively. However, the

Friday Morning, November 10, 2023

assumption of 90 degree contact angle in the HCM creates errors in the contact angle, particle size and adhesion energy when compared to the expectation of equilibrium shape.

Here, we will relax the assumption of hemispherical shape, and treat the more general case of spherical caps with any contact angle. We show that by simultaneously analyzing the data from metal vapor adsorption calorimetry (metal chemical potential versus coverage) and the data from He⁺ low-energy ion scattering spectroscopy or LEIS (signal versus coverage) within this new spherical cap model (SCM), we can determine the only contact angle that is consistent with both these sets of data. We then apply that approach to reanalyze all the metal / support systems which we had previously analyzed using the HCM to determine this self-consistent contact angle and the corresponding adhesion energy. These analyses rely on our recently developed SCM model for analyzing LEIS signals versus coverage which accounts for blocking of ion trajectories by particle material for any contact angle.¹ The resulting adhesion energies and contact angles are more accurate in predicting chemical potential versus size for all the metal / support systems. The trends of adhesion energy versus metal oxophilicity (for each oxide support) and carbophilicity (for carbon support) per unit area are also improved compared to earlier reports, and now better explain the support effect on the adhesion of metal nanoparticles.

Reference

1. Zhao, K.; Auerbach, D.; Campbell, C. T. Low Energy Ion Scattering Intensities from Supported Nanoparticles: The Spherical Cap Model. *J. Phys. Chem. C* 2023. <https://doi.org/10.1021/acs.jpcc.3c01175>

10:00am **HC+SS-FrM-6 Insights Into Adsorbate-Driven Surface Restructuring Using Size-Selected Pt/SiO₂ Nanoparticle Catalysts, Christopher O'Connor, T. Kim, C. Owen, Harvard University; N. Marcella, University of Illinois; A. Frenkel, Stony Brook University/Brookhaven National Laboratory; B. Kozinsky, C. Reece, Harvard University**

Heterogeneous catalysts are complex, dynamic materials that can undergo restructuring under reaction conditions. A key aspiration in the rationale design of catalysts is to tune performance (activity, selectivity, and stability) by using reactant conditions (composition, pressure, and temperature) and materials architecture to modify surface structure and composition. Herein, we investigate size-dependent catalyst restructuring under reactions conditions using a series of well controlled size-selected (1 – 8 nm) platinum nanoparticles supported on SiO₂ (Pt/SiO₂) as a model system. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements on 2 nm Pt/SiO₂ show that ~35% of CO adsorption sites are undercoordinated Pt under 1 mbar CO at 25 °C which is consistent with a regular truncated octahedral nanoparticle model. Under a CO environment, an incremental increase in temperature up to 350 °C induces restructuring to form a more undercoordinated surface indicated by a ~ 14% increase in total Pt sites for CO adsorption and ~ 75% undercoordinated surface sites. A thermal treatment at 350 °C under an inert atmosphere can reverse the catalyst structure to a well-coordinated surface, while cooling under a CO atmosphere can partially trap the surface in an undercoordinated structure. In contrast, 8 nm Pt/SiO₂ does not undergo significant restructuring from 25 to 350 °C under 1 mbar CO as evidenced by DRIFTS measurements. The experimental results are compared to theoretical calculations and molecular dynamics simulations to provide atomistic insight into the experimentally observed nanoparticle restructuring. This study clearly demonstrates that the adsorbate-driven surface restructuring of supported nanoparticle catalysts is strongly dependent on the reaction conditions (gas composition and temperature) and nanoparticle size, having broad implications for the structure of catalytically active surfaces under reaction conditions.

Author Index

Bold page numbers indicate presenter

— A —

Anderson, S.: HC+SS-FrM-4, **1**
Auerbach, D.: HC+SS-FrM-5, **1**

— B —

Brüner, P.: HC+SS-FrM-3, **1**

— C —

Campbell, C.: HC+SS-FrM-5, **1**

— F —

Frenkel, A.: HC+SS-FrM-6, **2**

— G —

Grehl, T.: HC+SS-FrM-3, **1**

— H —

Hong, W.: HC+SS-FrM-2, **1**

— J —

Jang, J.: HC+SS-FrM-2, **1**

Järvilehto, J.: HC+SS-FrM-3, **1**

Jeong, H.: HC+SS-FrM-2, **1**

— K —

Kim, D.: HC+SS-FrM-2, **1**

Kim, T.: HC+SS-FrM-6, **2**

Kozinsky, B.: HC+SS-FrM-6, **2**

— M —

Marcella, N.: HC+SS-FrM-6, **2**

Masubuchi, T.: HC+SS-FrM-4, **1**

Molina, D.: HC+SS-FrM-1, **1**

— O —

O'Brien, M.: HC+SS-FrM-4, **1**

O'Connor, C.: HC+SS-FrM-6, **2**

Oh, S.: HC+SS-FrM-2, **1**

Owen, C.: HC+SS-FrM-6, **2**

— P —

Park, J.: HC+SS-FrM-2, **1**

— R —

Reece, C.: HC+SS-FrM-6, **2**

— S —

Saedy, S.: HC+SS-FrM-3, **1**

— T —

Trenary, M.: HC+SS-FrM-1, **1**

— W —

Wang, Z.: HC+SS-FrM-4, **1**

— Z —

Zhao, K.: HC+SS-FrM-5, **1**